

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
PERSSON, M., et al

Serial No: 09/455,102

Filing Date: December 6, 1999

Title: POLYSILICATE MICROGELS

Asst. Commissioner of Patents
Washington, D.C. 20231



: Docket No: ANO5939P1US/3148

: Examiner: R. Lovering

: Group Art Unit: 1712

CERTIFICATE OF MAILING

I hereby certify that this correspondence
is being deposited with the United States
Postal Service as First Class Mail in an
envelope addressed to the Commissioner of
Patents and Trademarks, Washington, D.C.

20231 on March 16, 2001
Sonia V. Kulkarni

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Sir:

Enclosed herewith is the certified copy of European Patent Application No.
97850092.4 filed June 9, 1997 which is the priority document of the instant
application.

Respectfully submitted,

Lainie E. Parker/
Attorney for Applicants
Reg. No. 36,123

Akzo Nobel Inc.
Intellectual Property Department
7 Livingstone Avenue
Dobbs Ferry, New York 10522
(914) 674-5466

8 3/22/01



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

97850092.4

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

Der Präsident des Europäischen Patentamts:
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

W.G.F. VAN ROSMALEN



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

Anmeldung Nr.:
Application no.: 97850092.4
Demande n°:

Anmeldetag:
Date of filing: 09/06/97
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
AKZO NOBEL N.V.
6800 SB Arnhem
NETHERLANDS
Eka Chemicals AB
445 80 Bohus

SWEDEN
Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Polysilicate microgels

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

C01B33/143, D21H21/10, D21H17/68, C02F1/52

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

Polysilicate microgels

The present invention generally relates to polysilicate microgels. More particularly, the invention relates to polysilicate microgels, their preparation and use in paper making and water purification.

5 Background

Polysilicate microgels, optionally aluminated, are known in the art as drainage and retention aids in the manufacture of paper and similar cellulosic products. The microgels comprise solutions or dispersions of very small primary silica-based particles, usually with a size of from 1 to 2 nm in diameter, having a high specific surface area,
10 typically at least about 1000 m²/g, which are linked together into individual chains to form three-dimensional network structures.

The preparation of polysilicate and aluminated polysilicate microgels generally comprises acidifying a dilute aqueous solution of alkali metal silicate by using an acid or acid ion-exchanger, ageing the acidified mixture and then further diluting the aged
15 mixture to a silica concentration of not greater than 2% by weight. The silica-based microgels normally have poor stability and the high dilution is normally necessary to avoid gelation of the microgels. Because of the stability problems associated with these products, and the prohibitive cost of shipping stable, but extremely dilute, solutions containing about 0.5% by weight or less of silica, the polysilicate microgels are preferably prepared at the
20 location of intended use, for example at the paper mill. Production units or generators for continuously preparing polysilicate microgels that are installable at the paper mill are known in the art. Hereby the microgels obtained can be prepared and continuously introduced into the stock containing cellulosic fibres and filler to be drained. However, any disturbance in the production unit, for example variations in quality and/or quantity of the
25 microgel produced, will change the drainage and retention performance of the product which may adversely affect the paper making process, thereby producing cellulosic products of uneven quality.

The Invention

In accordance with the present invention it has been found that polysilicate
30 microgels can be prepared in a very advantageous manner by mixing an alkaline alkali metal silicate with a silica-based material. Hereby it is possible to prepare high-concentration polysilicate and aluminated polysilicate microgels and microgel precursors. More specifically, this invention concerns a process for preparing an aqueous polysilicate microgel which comprises mixing an aqueous solution of alkali metal silicate with an
35 aqueous phase of silica-based material preferably having a pH of 11 or less. The invention

thus relates to a process for preparing polysilicate microgels, polysilicate microgels per se and their use, as further defined in the claims.

5 The polysilicate microgels of this invention exhibit very high stability and can be easily prepared and shipped at considerably higher silica concentrations as compared to previously known polysilicate microgels. High-concentration polysilicate microgels of this invention can be prepared under controlled conditions in a plant intended for such produc-
tion and shipped as a concentrated product to the paper mill in an economically attractive
manner. Hereby there will be no need for installing production units or generators for
preparing polysilicate microgel drainage and retention aids at a large number of paper
10 mills, thereby offering substantial technical and economic benefits.

If desired, the high-concentration polysilicate microgel of this invention can be
diluted with water or an aqueous acid solution before being used, for example as a drainge
and retention aid in papermaking, in order to facilitate dosage of the silica-based material
to the dilute fibre stock. In this respect, the high-concentration polysilicate microgel of the
15 invention can be regarded as a precursor for low-concentration polysilicate microgels
which can be formed by the addition of water, optionally acidified. In this application, a
storage tank for the high-concentration polysilicate microgel can be installed at the location
of intended use, which is more attractive economically than installing a complete
polysilicate microgel production unit or generator. Of course, low-concentration polysilicate
20 microgels can also be formed in situ in the aqueous phase into which the high-
concentration silica-based product is being incorporated as a performance additive, for
example by adding the high-concentration product to a cellulosic fibre suspension to be
drained in papermaking or to waste water to be purified. This application using high-
concentration polysilicate microgels of this invention as a precursor for in situ formation of
25 low-concentration polysilicate microgels represents a significant progress in the art.

The alkali metal silicate used to prepare the polysilicate microgels according
to the invention can be any water-soluble silicate salt such as sodium or potassium silicate
or sodium or potassium water glass. These are available with varying molar ratios of SiO_2
to Na_2O or K_2O and the molar ratio is usually within the range of from 1.5:1 to 4.5:1, most
30 often from about 2.5:1 to 3.9:1. The alkali metal silicate preferably is a sodium silicate.
Aqueous solutions of alkali metal silicate are alkaline and usually have a pH of about 13 or
above 13. The alkali metal silicate solution usually have a silica concentration within the
range of from 5 to 35% by weight, suitably above 10% by weight and preferably within the
range of from 15 to 30% by weight.

35 Silica-based material that can be mixed with the alkali metal silicate solution
according to the invention can be selected from a wide variety of siliceous materials

including dispersed silicas such as, for example, silica-based sols, fumed silica, silica gels, precipitated silicas, acidified solutions of alkali metal silicates, and suspensions of silica-containing clays of smectite-type. The aqueous solution of silica-based material can have a pH within the range of from 1 to 11. In one preferred aspect of this invention, the pH of the aqueous silica-based material is within the range of from 1.5 to 4. In another preferred aspect of this invention, the pH of the aqueous silica-based material is within the range of from 4 to 11.0 and preferably within the range of from 4.5 to 10.6. In yet another preferred aspect of this invention, the pH of the aqueous silica-based material is within the range of from 7 to 11.0.

In one preferred embodiment of this invention, the silica-based material used for mixing with the alkali metal silicate solution is a silica-based sol, suitably an alkali-stabilized silica sol. Sols of this type are known in the art and generally comprise an aqueous phase and particles based on silica, i.e. SiO_2 . It is preferred that the particles are colloidal, i.e. in the colloidal range of particle size. Particles of this type include colloidal silica, colloidal aluminium-modified silica and colloidal aluminium silicate. The silica-based sols, such as the alkali-stabilized ones, usually have a pH within the range of from about 4 to about 11, suitably at least 6.5 and preferably from 8 to 10.6. Suitable sols with silica-based particles include those disclosed in U.S. Pat. Nos. 4,388,150; 4,961,825; 4,980,025; 5,368,833; 5,447,604; and 5,603,805; the teachings of which are incorporated herein by reference.

The silica-based particles contained in the sol can have an average particle size less than about 100 nm and suitably less than about 50 nm. In a preferred embodiment of the invention, the silica-based sol particles can have an average particle size of less than about 30 nm and preferably within the range of from about 1 to about 15 nm. As conventional in silica chemistry, the size refers to the average size of the primary particles, which may be aggregated or non-aggregated. The silica-based particles present in the sol should suitably have a specific surface area of at least $50 \text{ m}^2/\text{g}$. The specific surface area can be measured by means of titration with NaOH in known manner, e.g. as described by Sears in Analytical Chemistry 28(1956):12, 1981-1983 and in U.S. Pat. No. 5,176,891. The given area thus represents the average specific surface area of the particles. Suitably the specific surface area is within the range of from 50 to $1200 \text{ m}^2/\text{g}$ and preferably from 70 to $1000 \text{ m}^2/\text{g}$.

The silica-based sols used in the process suitably have a pH within the range of from 6.5 to 11 and a SiO_2 content within the range of from 5 to 60% by weight, preferably a pH within the range of from 8 to 10.6 and SiO_2 content within the range of from 10 to 50% by weight.

In another preferred embodiment of this invention, the silica-based material used for mixing with the alkali metal silicate solution is an acidified alkali metal silicate. Suitable acidified alkali metal silicates include polysilicic acid, polymeric silicic acid, active silica and polysilicate microgels, optionally aluminated. In the art, the term polysilicate microgel is often used interchangeably with active, or activated, silica to define the same type of microparticulate silica-based product. The acidified alkali metal silicate solution can be prepared from any water-soluble silicate salt such as sodium or potassium silicate or sodium or potassium water glass. The acidified alkali metal silicate preferably is prepared from a sodium silicate. Alkali metal silicates that can be used to prepare the acidified silicate solution are available with varying molar ratios of SiO_2 to Na_2O or K_2O and the ratio is usually within the range of from 1.5:1 to 4.5:1, most often from about 2.5:1 to 3.9:1. The acidified alkali metal silicate solution can have a pH from 1 to 11. In one preferred aspect of this embodiment, the pH of the acidified silicate solution is within the range of from 1.5 to 4. In another preferred aspect of this embodiment, the pH of the acidified silicate solution is within the range of from 4 to 11 and preferably within the range of from 4.5 to 10.6. In yet another preferred aspect of this embodiment, the pH of the acidified silicate solution is within the range of from 7 to 11.

The acidified alkali metal silicate solution can be prepared by acidifying an aqueous solution of alkali metal silicate which suitably contains about 0.1 to 6 % by weight of SiO_2 . Acidification can be carried out in many ways, for example by using acid ion-exchange resins, mineral acids, e.g. sulphuric acid, hydrochloric acid or phosphoric acid, acid salts or acid gases, suitably ion-exchangers or mineral acids or a combination thereof, optionally in combination with an aluminium salt. Where higher ratios of SiO_2 to Na_2O are desired, it is preferred to use acid ion-exchangers. The acidification is accordingly carried out to a pH within the range of from 1 to 11. In one preferred aspect of this embodiment, the acidification is thus carried out to a pH within the acid range of from 1.5 to 4. In other preferred aspects of this embodiment, the acidification is carried out to a pH within the range of from 4 to 11 and preferably to a pH within the range of from 4.5 to 10.6. In yet another preferred aspect of this embodiment, partial acidification is carried out to a pH of from about 7 to 11. Suitable acidified alkali metal silicates for use as starting materials in the process of this invention include those disclosed in U.S. Pat. Nos. 4,388,150; 4,954,220; 5,127,994; 5,279,807; 5,312,595; and 5,503,820; the teachings of which are incorporated herein by reference.

Acidified alkali metal silicate solutions that can be used for mixing with the alkaline alkali metal silicate solution in order to prepare the high-concentration polysilicate microgel of this invention can also be selected from alkali metal silicates that have been both acidified and aluminated. The alumination can be carried out simultaneously with the

acidification, for example as disclosed in U.S. Pat. Nos. 5,470,435; 5,482,693; 5,543,014; and 5,626,921, or after the acidification, for example as disclosed in U.S. Pat. No. 5,176,891. In the art, aluminated low-concentration polysilicate microgels are also referred to as polyaluminosilicates and polyaluminosilicate microgels. Suitable aluminated and acidified alkali metal silicates for use as starting materials in the process of this invention include the aluminated polysilicate microgels disclosed in the above-mentioned U.S. patents, the teachings of which are also incorporated herein by reference.

Acidified, and optionally aluminated, alkali metal silicates for use in the process of this invention suitably have a high specific surface area, suitably above about 1000 m²/g. The specific surface area can be within the range of from 1000 to 1700 m²/g, preferably from 1050 to 1600 m²/g. The specific surface area can be measured as described above. The acidified alkali metal silicates can be in the form of microparticulate silica comprising very small 1-2 nm diameter particles which are linked together in chains and networks to form three-dimensional structures, and optionally aluminated.

The process of this invention comprises mixing the alkaline alkali metal silicate with the silica-based material. The mixing can be conducted at a temperature of from 0 to 300°C, suitably from 5 to 150°C and preferably from about 10 to about 100°C. The process can be carried out by adding the silica-based material to the aqueous solution of alkali metal silicate with stirring. Preferably the silica-based material is slowly added to the alkali metal silicate under vigorous mixing. The solution of silica-based material can have a silica concentration within the range of from 0.1 to 60% by weight, depending on the type of material used. When using silica-based sols such as alkali-stabilized sols, the SiO₂ content can be from 5 to 60% by weight, preferably from 10 to 50% by weight. When using acidified alkali metal silicates as described herein, the SiO₂ content can be from 0.1 to 10% by weight, preferably from 0.5 to 6% by weight. The SiO₂ present in the polysilicate microgels obtained thus originates from both the alkali metal silicate and the silica-based material. The mixing can be carried out such that from 5 to 95% by weight and suitably from 15 to 85% by weight of SiO₂ present in the polysilicate microgel is derived from the alkali metal silicate, and 95 to 5% by weight and suitable from 85 to 15% of SiO₂ present in the polysilicate microgel is derived from the silica-based material.

If desired, additional compounds can be incorporated into the mixture obtained in the process. Suitable additional compounds include various salts such as, for example, aluminium salts and other metal salts, and various acids. These additional compounds may have a positive effect on storage stability and/or on the drainage and/or retention performance of the microgels. Suitable aluminium salts include alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium

chlorides, polyaluminium sulphates, polyaluminium compounds containing both chloride and sulphate ions, polyaluminium silicate-sulphates, and mixtures thereof. The polyaluminium compounds may also contain other anions, for example anions from phosphoric acid, organic acids such as citric acid and oxalic acid. Preferred aluminium salts include aluminates, e.g. sodium or potassium aluminate, preferably sodium aluminate. Aluminium salts can be incorporated into the polysilicate microgels in an amount corresponding to a $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio within the range of from 1500:1 to 5:1 and suitably from 750:1 to 6:1. Suitable metal salts other than Al include those based on alkali metals and alkaline earth metals such as, for example, Li, K, Mg and Ca. These additional compounds are generally incorporated in amounts such that the ratio of Na to such additional metal present in the metal salt is higher than 1, preferably higher than 5. Suitable acids include organic acids, preferably diacids such as dicarboxylic and disulphonic acids, e.g. oxalic, malonic, succinic, glutaric and adipic acid, and organic polyacids, such as polymers containing carboxylic acid and sulphonic acid groupss, such as polyacrylic acid. The additional acid is suitably incorporated in the polysilicate microgels in an amount sufficient to give a positive effect on stability, suitably up to 10% by weight. Even if arbitrary order of mixing or addition can be used, it is generally preferred that these additional compound be incorporated in the mixture of alkali metal silicate and silica-based material. A further preferred order of mixing is to add the acid to the acidified solution of alkali metal silicate prior to mixing with the alkali metal silicate solution.

The resulting aqueous solution or dispersion of polysilicate microgel, or microparticulate silica-based material, normally have a SiO_2 content of a least 5% by weight. The SiO_2 content may depend on several factors such as, for example, the starting materials used and their SiO_2 content, the incorporation of aluminium salts, etc. Suitably the SiO_2 content is at least 10% by weight, preferably at least 15% by weight and most preferably at least 17.5% by weight. The upper limit is usually about 50% by weight, suitably about 35% by weight and in most cases about 30% by weight. If desired, the aqueous polysilicate microgel can be concentrated after preparation. This can be advantageous so as to provide higher concentration polysilicate microgels which may lead to further reduction of shipping costs. Concentration can be carried out by known methods, for example by membrane processes or evaporation of water.

The polysilicate microgel obtained can have a molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ within the range of from 3:1 to 50:1, suitably from 4:1 to 30:1 and preferably from 5:1 to 20:1. This ratio may depend on several factors such as, for example, type of starting materials, type of acidification of starting materials, additional metal salts, etc. The same applies the molar ratio of $\text{SiO}_2:\text{M}_2\text{O}$, where M is alkali metal, e.g. Li, Na, K and mixtures thereof. The

polysilicate microgel can have a molar ratio of $\text{SiO}_2\text{:M}_2\text{O}$ within the range of from 2:1 to 50:1, suitably from 2.2:1 to 30:1 and preferably from 3:1 to 20:1. The obtained aqueous silica-based microparticulate material generally have a pH below 14, suitably below 13 and preferably below 12. The pH is suitably above 9.

5 The high-concentration polysilicate microgel of this invention can be diluted or mixed with aqueous solutions or suspensions before use or at use. Hereby low-concentration polysilicate microgels can be formed and the high-concentration polysilicate microgel of the invention can thus be used as a precursor for low-concentration polysilicate microgels. In a preferred embodiment, the high-concentration polysilicate microgel is mixed
10 with an aqueous solution or suspension having a pH lower than that of the high-concentration microgel whereby the high-concentration microgel undergoes a pH transition. Suitable aqueous solutions and suspensions include those containing acids, cellulosic fibres and optional filler, and acid aluminium salts.

 The polysilicate microgel obtained by the process can be described as a
15 silica-based microparticulate material comprising very small particles, preferably 1-2 nm in diameter, which are linked together in chains or networks to form three-dimensional structures. The aqueous polysilicate microgels may also contain larger particles depending on, inter alia, the starting materials used in the preparation of the microgels. The specific surface area of the silica-based microparticles, the microgel, suitably is at least $1000 \text{ m}^2/\text{g}$.
20 Methods for measuring the specific surface area are described hereinabove.

 The polysilicate microgels of this invention are suitable for use as flocculating agents, for example in the production of pulp and paper and within the field of water purification, both for purification of different kinds of waste water and for purification specifically of white water from the pulp and paper industry. The polysilicate microgels can be used
25 as flocculating agents in combination with organic polymers which can be selected from anionic, amphoteric, nonionic and cationic polymers and mixtures thereof. The use of such polymers as flocculating agents is well known in the art. The polymers can be derived from natural or synthetic sources, and they can be linear or branched. Examples of generally suitable polymers include anionic, amphoteric and cationic starches, anionic, amphoteric and
30 cationic guar gums, and anionic, amphoteric and cationic acrylamide-based polymers, as well as cationic poly(diallyldimethyl ammonium chloride), cationic polyethylene imines, cationic polyamines and polyamidoamines, melamine-formaldehyde and urea-formaldehyde resins. Suitably the polysilicate microgel is used in combination with at least one cationic or amphoteric polymer, preferably cationic polymer. Cationic starch and cationic polyacrylamide
35 are particularly preferred polymers and they can be used singly, together with each other or together with other polymers, e.g. other cationic polymers or anionic polyacrylamide. Even if

arbitrary order of addition can be used, it is preferred that the polymer or polymers be added to pulp, stock or water before the polysilicate microgels.

The preferred field of use for the polysilicate microgels, in combination with polymer as described above, is for improvement of drainage and/or retention in the manufacture of paper, i.e. the use as drainage and/or retention aids in papermaking. The present invention further relates to a process for the production of paper from a suspension of cellulosic fibres, and optional fillers, which comprises adding to the suspension at least one cationic or amphoteric organic polymer and polysilicate microgel as described herein, forming and draining the suspension on a wire. The invention thus relates to a process as further defined in the claims.

When using the polysilicate microgels in combination with organic polymer(s) as mentioned above, it is further preferred to use at least one anionic trash catcher (ATC). ATC's are known in the art as neutralizing agents for detrimental anionic substances present in the stock. Hereby ATC's can enhance the efficiency of other additives used in the process. Accordingly, further suitable combinations of polymers that can be co-used with the polysilicate microgels of this invention include ATC in combination with high molecular weight polymer(s), e.g. cationic starch and/or cationic polyacrylamide, anionic polyacrylamide as well as cationic starch and/or cationic polyacrylamide in combination with anionic polyacrylamide. Suitable ATC's include cationic polyelectrolytes, especially low molecular weight highly charged cationic organic polymers such as polyamines, polyethyleneimines, homo- and copolymers based on diallyldimethyl ammonium chloride, (meth)acrylamides and (meth)acrylates. Normally, ATC's are added to the stock prior to other polymer(s). Alternatively, the ATC polymer can be added simultaneously with the other polymer(s), either separately or in admixture, for example as disclosed in European Pat. Appl. Publ. No. 752496, the teaching of which is incorporated herein by reference. Mixtures comprising ATC polymer and high molecular weight cationic polymer are particularly preferred.

The amount of polysilicate microgel added to the stock, or suspension of cellulosic fibres, may vary within wide limits depending on, among other things, type of stock, type of polysilicate microgel used. The amount usually is at least 0.01 kg/ton and often at least 0.05 kg/ton, calculated as SiO_2 and based on dry stock system, i.e. cellulosic fibres and optional fillers. The upper limit can be 8 kg/ton and suitably is 5 kg/ton. Usually the polysilicate microgel dosage is within the range of from 0.1 to 2 kg/ton.

The dosage of organic polymer to the stock can be varied over a broad range depending on, among other things, the type of polymer or polymers used and whether other effects are desired, e.g. wet and dry paper strength. Usually, there is used at least 0.005 kg of polymer per ton of dry fibres and optional fillers. For synthetic cationic polymers, such as

for example cationic polyacrylamide, amounts of at least 0.005 kg/ton are usually used, calculated as dry on dry fibres and optional fillers, suitably from 0.01 to 3 and preferably from 0.03 to 2 kg/ton. For cationic polymers based on carbohydrates, such as cationic starch and cationic guar gum, amounts of at least 0.05 kg/ton, calculated as dry on dry fibres and optional fillers, are usually used. For these polymers the amounts are suitably from 0.1 to 30 kg/ton and preferably from 1 to 15 kg/ton.

In a preferred embodiment of this invention, the polysilicate microgels are used as drainage and/or retention aids in combination with at least one organic polymer, as described above, and at least one aluminium compound. Aluminium compounds can be used to further improve the drainage and/or retention performance of stock additives comprising polysilicate microgels and aluminated polysilicate microgels. Suitable aluminium salts include alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates, polyaluminium compounds containing both chloride and sulphate ions, polyaluminium silicate-sulphates, and mixtures thereof. The polyaluminium compounds may also contain other anions, for example anions from phosphoric acid, organic acids such as citric acid and oxalic acid. Preferred aluminium salts include sodium aluminate, alum and polyaluminium compounds. The aluminium compound can be added before, simultaneously with or after the addition of the polysilicate microgel. In many cases, it is often suitable to add the aluminium compound to the stock early in the process, for example prior to the other additives. Alternatively, or additionally, the aluminium compound can be added simultaneously with the polysilicate microgel, either separately or in admixture with it, for example as disclosed in European Pat. Appl. Publ. No. 748897, the teachings of which is incorporated herein by reference. Adding the polysilicate microgels and aluminium compound simultaneously to the stock represent a preferred embodiment of the invention.

The amount of aluminium compound added to the suspension may depend on the type of aluminium compound used and whether other effects are desired. It is for instance well-known in the art to utilize aluminium compounds as precipitants for rosin-based sizes. The amount of aluminium compound added to the stock should suitably be at least 0.001 kg/ton, calculated as Al_2O_3 and based on dry fibres and optional fillers. Suitably the amount is within the range of from 0.01 to 5 kg/ton and preferably within the range from 0.05 to 1 kg/ton.

The papermaking process according to the invention can be used for producing cellulosic products in sheet or web form such as for example pulp sheets and paper. It is preferred that the process is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other sheet or

web-like products, such as for example board and paperboard, and the production thereof. The papermaking process according to the invention can be used in the production of sheet or web-like products from different types of suspensions containing cellulosic fibres and the suspension, or stock, should suitably contain at least 50% by weight of such fibres, based on dry substance. The suspension can be based on fibres from chemical pulp, such as sulphate and sulphite pulp, thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp or groundwood pulp from both hardwood and softwood, and can also be used for suspensions based on recycled fibres. The suspension can also contain mineral fillers of conventional types, such as for example kaolin, titanium dioxide, gypsum, talc and both natural and synthetic calcium carbonates. The suspension can have a pH within the range from about 3 to about 10. The pH is suitably above 3.5 and preferably within the range of from 4 to 9. The stock can of course also contain papermaking additives of conventional types, such as wet-strength agents, stock sizes based on rosin, ketene dimers or alkenyl succinic anhydrides, and the like.

The invention is further illustrated in the following Examples which, however, are not intended to limit same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

Example 1

Polysilicate microgels of this invention were prepared by slowly adding a silica-based sol to sodium water glass (hereafter Na silicate) having a SiO_2 content of about 28% by weight and a weight ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of about 3.3 at 50°C under vigorous stirring. In some tests, an additional alkali metal salt, either potassium borate (KBO_2 (aq); 57% active) and/or lithium hydroxide (LiOH (aq); 97% $\text{LiOH}\cdot\text{H}_2\text{O}$), was introduced into the mixture thus obtained. The silica-based sols used were the following:

A: A sol of colloidal silica having a SiO_2 content of 40% by weight and containing silica particles with a specific surface area of $220 \text{ m}^2/\text{g}$. This sol is commercially available under the tradename Bindzil™ 40/220, Eka Chemicals.

B: A sol of colloidal silica of the type described in U.S. Pat. No. 4,388,150. The sol was alkali-stabilized to a molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of about 40, had a pH of about 8-9 and a SiO_2 content of about 15% by weight and contained silica particles with a specific surface area of about $500 \text{ m}^2/\text{g}$.

C: A sol of aluminium-modified silicic acid of the type described in U.S. Pat. Nos. 4,961,825 and 4,980,025. The sol had a pH of about 8-9 and a SiO_2 content of about 15% by weight and contained silica particles with a specific surface area of about $500 \text{ m}^2/\text{g}$.

D: A sol of colloidal silica having a SiO₂ content of 30% by weight and containing silica particles having a specific surface area of 220 m²/g and being surface-modified with aluminium to a degree of 5%. This sol is commercially available under the tradename Bindzil™ 305, Eka Chemicals.

- 5 Table I below shows the amounts (Amt.(g)) of starting materials used in the process, and the weight ratios of SiO₂:Na₂O and SiO₂:M₂O (SiO₂:Na₂O/SiO₂:M₂O) where M is alkali metal (Na+K+Li), and the content of SiO₂, in % by weight (SiO₂ (%)), of the polysilicate microgel obtained.

Table I

10	Product No.	Na silicate Amt.(g)	SiO ₂ sol Type/Amt.(g)	KBO ₂ (aq) Amt (g)	LiOH (aq) Amt.(g)	SiO ₂ :Na ₂ O/ SiO ₂ :M ₂ O	SiO ₂ (%)
	SP2-3	500	A/180	30.4	18.9	5.0/3.4	26.5
	SP2-4	500	A/180	-	18.9	5.0/3.8	26,5
	SP2-5	400	A/231	29.5	18.4	6.0/3.8	26.5
15	SP2-6	400	A/231	-	18.4	6.0/4.3	26.5
	SP2-7	300	B/319	18.8	11.7	5.0/3.4	19.5
	SP2-8	300	B/319	-	11.7	5.0/3.8	19.5
	SP2-9	500	B/150	-	-	3.8/3.8	24.1
	SP2-10	500	A/180	30.4	18.9	5.0/3.4	23.0
20	SP2-11	500	A/180	-	18.9	5.0/3.8	23.0
	SP2-12	400	A/231	29.5	18.4	6.0/3.8	23.0
	SP2-13	400	A/231	-	18.4	6.0/4.3	23.0
	SP2-15	300	C/325	-	11.7	5.0/3.8	19.4
	SP2-16	300	C/325	-	17.2	5.0/3.4	16.1
25	SP2-17	300	C/325	-	11.7	5.0/3.8	19.0
	SP2-18	500	C/153	-	-	3.8/3.8	19.6
	SP2-19	100	C/61	-	3.3	4.3/3.4	20.3
	SP2-20	100	C/99	-	6.0	4.9/3.3	17.1
	SP2-23	300	D/142	18.2	11.3	5.0/3.4	13.4

30

Example 2

Stability of polysilicate microgels prepared according to Example 1 was evaluated by measuring the viscosity 1, 3, 5 or 10 days after preparation. The viscosity measurements were made at 20°C with a Brookfield viscosimeter model RTV, spindle 61, 60 rpm.

- 35 The results are set forth in Table II.

Table II

	Polysilicate microgel	SiO ₂ (%)	Viscosity (cP) at 20°C			
			1 day	3 days	5 days	10 days
	SP2-7	19.5	-	14	14	13
5	SP2-8	19.5	-	11	11	11
	SP2-9	24.1	-	55	58	61
	SP2-10	23.0	29	-	52	-
	SP2-11	23.0	19	-	28	-
	SP2-13	23.0	27	-	34	-
10	SP2-15	13.9	11	-	6	-
	SP2-16	16.1	6	-	6	-
	SP2-17	19.0	7	-	7	-
	SP2-18	19.6	12	-	12	-

15 Example 3

In the following tests, drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden, which measures the time for draining a set volume of stock through a wire when removing a plug and applying a vacuum to that side of the wire opposite to the side on which the stock is present.

20 The drainage tests were made using an alkaline stock at pH 8.0 and 0.25% consistency containing cellulosic fibres (60% bleached birch/40% pine sulphate) and 30% of chalk to which stock 0.3 g/l of Na₂SO₄·10H₂O was added. In the tests, polysilicate microgels according to Example 1 were tested in conjunction with a cationic polymer, Raisamyl 142, which is a conventional medium-high cationized starch having a degree of substitution of

25 0.042, hereafter also referred to as CS, which was added to the stock in an amount of 12 kg/ton, calculated as dry on dry stock system, and an aluminium salt, sodium aluminate, which was added in an amount of 0.2 kg/ton, calculated as Al₂O₃ and based on dry stock system. The product used for comparison was a sol of silica-based particles of the type disclosed in U.S. Pat. No. 5,368,833. The sol had an S-value of about 25% and contained silica

30 particles with a specific surface area of about 900 m²/g which were surface-modified with aluminium to a degree of 5%, hereinafter referred to as Sol 1.

The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test and chemical additions to the stock were conducted as follows:

- i) adding cationic starch followed by stirring for 30 seconds,
- 35 ii) adding polysilicate microgels and aluminium salt simultaneously but separately, or adding comparison silica-based product, followed by stirring for 15 seconds,

iii) draining the stock while automatically recording the drainage time.

Table III shows the drainage results obtained when using varying dosages of different types of silica-based material where dosages are in kg/ton, calculated as SiO_2 and based on dry stock system; shorter drainage times means better drainage performance of the additives. Without addition of chemicals, the stock had a drainage time of 19.5 sec.

Table III

Silica-based		Drainage time (sec) at SiO_2 dosage of				
	material	0.5 kg/t	0.8 kg/t	1.2 kg/t	1.7 kg/t	2.2 kg/t
	Sol 1	13.0	10.9	9.1	7.7	6.5
10	SP2-7	15.0	10.5	8.7	7.2	6.2
	SP2-8	16.5	12.3	9.9	9.1	8.9
	SP2-9	15.2	14.5	12.8	12.0	12.0
	SP2-10	14.3	10.9	8.0	6.5	6.2
	SP2-13	14.6	10.3	8.2	7.5	7.7
15	SP2-16	17.2	15.0	13.1	11.5	10.7

Example 4

In this test series, retention was evaluated by means of the DDA used in Example 3 in combination with a nephelometer. First pass retention was evaluated by measuring the turbidity of the filtrate, the white water, obtained by draining the stock. Additives and addition order according to Example 3 were similarly used in this test series.

Table IV shows the retention effect measured as turbidity of white water obtained by dosing varying amounts of different types of silica-based material where dosages are in kg/ton, calculated as SiO_2 and based on dry stock system. Without addition of chemicals, the stock had a turbidity of 93 NTU.

Table IV

Silica-based		Turbidity [NTU] at SiO_2 dosage of			
	material	0.8 kg/t	1.2 kg/t	1.7 kg/t	2.2 kg/t
30	Sol 1	53	48	43	-
	SP2-7	62	56	48	48
	SP2-8	73	61	62	60
	SP2-10	69	55	52	48
	SP2-13	65	60	55	54

Example 5

Polysilicate microgels of this invention were prepared by mixing at room temperature sodium water glass (hereafter Na silicate) having a SiO_2 content of about 23% by weight and a weight ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of about 3.3 with an acid ion-exchanger treated sodium silicate solution (Acid SiO_2) having a SiO_2 content of about 5-6% by weight and pH of about 2.5 to achieve a mixture with a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of about 4.0. In some tests, this mixing was followed by slowly adding a sodium aluminate solution (NaAl (aq)) containing about 2.5% by weight of Al_2O_3 under vigorous stirring. In some tests, an aqueous solution of additional alkaline earth salt was introduced into the mixture thus obtained, either magnesium acetate (M; 1.5% $\text{Mg}(\text{acetate})_2$) or calcium nitrate (C; 2.5% $\text{Ca}(\text{NO}_3)_2$).

Table V shows the amounts (Amt.(g)) of the starting materials used in the process, and the pH and silica content, in % by weight, of the polysilicate microgels obtained.

Table V

Product No.	Na silicate Amt. (g)	Acid SiO_2 Amt. (g)	Na Al (aq.) Amt (g)	Salt (aq) Type/Amt.(g)	pH	SiO_2 (%)
SAV-5-1	320	237	34.3	-	11.3	18.8
SAV-6-1	209	1248	-	-	10.3	7.6
SAV-6-2	200	260	-	-	10.4	13.0
SAV-9-3	140	250	-	M/57	10.9	12.1
SAV-11-2	129	100	-	C/21	11.5	13.9

Example 6

In this Example, the polysilicate microgels according to Example 5 were tested for drainage performance as in Example 3 using a similar stock of pH 8.4. The cationic starch, standard silica sol, aluminium salt, dosages and order of addition as used in Example 3 were similarly used in these tests.

Table VI shows the drainage results by using different types of silica-based materials varying amounts, in kg/ton, calculated as SiO_2 and based on dry stock system. Without addition of chemicals, the drainage time of the stock was 21.2 sec.

Table VI

Silica-based material	Drainage time (sec) at SiO_2 dosage of			
	0.5 kg/t	0.8 kg/t	1.2 kg/t	1.7 kg/t
Sol 1	12.5	10.5	9.0	7.5
SAV-5-1	15.2	12.0	11.6	7.9
SAV-9-3	13.9	11.1	9.9	7.5
SAV-11-2	15.7	11.1	9.7	7.0

Example 7

Polysilicate microgels according to Example 5 was tested for retention performance by measuring the turbidity of the white water obtained by draining the stocks according to Example 6. Retention was evaluated according to the procedure of Example 4. Without addition of chemicals, the stock had a turbidity of 104 NTU.

Table VII shows the results obtained.

Table VII

Silica-based material	Turbidity [NTU] at SiO ₂ dosage of		
	0.5 kg/t	0.8 kg/t	1.2 kg/t
Sol 1	66	59	51
SAV-5-1	84	74	66
SAV-9-3	82	70	62
SAV-11-2	81	72	64

Example 8

Polysilicate microgels according to Example 5 were tested for drainage performance as in Example 6 except that the aluminium salt used was a polyaluminium chloride, Redifloc 8210, which was added in an amount of 0.2 kg/ton, calculated as Al₂O₃ and based on dry stock system.

The results are set forth in Table VIII

Table VIII

Silica-based material	Drainage time (sec) at SiO ₂ dosage of			
	0.5 kg/t	0.8 kg/t	1.2 kg/t	1.7 kg/t
Sol 1	12.5	10.5	9.0	7.5
SAV-5-1	15.9	12.6	11.1	9.0
SAV-6-2	14.7	11.0	9.3	7.5
SAV-9-3	14.7	11.3	9.6	7.8
SAV-11-2	14.5	11.2	9.7	7.7

Example 9

Polysilicate microgels according to Example 5 was tested for retention performance by measuring the turbidity of the white water obtained by draining the stocks according to Example 8. Retention was evaluated according to the procedure of Example 4. Without addition of chemicals, the stock had a turbidity of 104 NTU.

Table IX shows the results obtained.

Table IX

	Silica-based material	Turbidity [NTU] at SiO ₂ dosage of		
		0.5 kg/t	0.8 kg/t	1.2 kg/t
5	SAV-5-1	87	73	66
	SAV-6-2	86	75	64
	SAV-9-3	88	76	66
	SAV-11-2	89	70	65

10 Example 10

A polysilicate microgel according to Example 5, SAV-6-1, was tested for drainage performance as in Example 6 using a similar stock at pH 8.0 except that varying amounts (Amt.(kg/t)) of sodium aluminate (Aluminate), calculated as Al₂O₃ and based on dry stock system, were used. Without addition of chemicals, the drainage time of the stock was 20.5 sec.

The results are set forth in Table X.

Table X

	Silica-based material	Aluminate Amt.(kg/t)	Drainage time (sec) at SiO ₂ dosage of			
			0.3 kg/t	0.6 kg/t	1.0 kg/t	2.0 kg/t
20	Sol 1	-	16.0	13.0	10.0	8.0
	Sol 1	0.1	13.5	10.5	9.0	6.0
	Sol 1	0.25	-	7.5	-	5.5
	SAV-6-1	-	17.0	14.0	11.0	9.5
25	SAV-6-1	0.05	12.0	8.5	7.5	5.5
	SAV-6-1	0.1	12.0	8.5	7.0	4.5
	SAV-6-1	0.25	-	8.0	6.5	4.0

Example 11

30 Retention performance was tested by measuring the turbidity of the white water obtained by draining stocks according to Example 10 where no aluminate was added to the stock. Retention was evaluated according to the procedure of Example 4. Without addition of chemicals, the stock had a retention of 98 NTU.

Table XI shows the results.

Table XI

Silica-based material	Turbidity [NTU] at SiO ₂ dosage of				
	0.3 kg/t	0.6 kg/t	1.0 kg/t t	1.5 kg/t	2.0 kg/t
Sol 1	74	63	55	50	47
5 SAV-6-1	83	68	62	-	52

Example 12

Aluminated polysilicate microgels according to the invention were prepared by mixing sodium water glass with a SiO₂ content of about 23% by weight and weight ratio SiO₂:Na₂O of about 3.3 with an acid ion-exchanger treated sodium silicate solution having a SiO₂ content of about 5-6% by weight and pH of about 2.5 to achieve a mixture having a weight ratio SiO₂:Na₂O of about 10:1 followed by addition of a dilute sodium aluminate solution (NaAl (aq)) containing about 2.5% by weight of Al₂O₃ under stirring. The aqueous mixture thus obtained was ion-exchanged by means of an acid ion-exchanger to pH about 6 and then concentrated by evaporation of water to a final stabilized, microparticulate silica-based material having a SiO₂ content above 10% by weight.

Table XII shows the SiO₂ and Al₂O₃ contents of the products obtained as well as their stability and pH. Stability was evaluated visually about 1 week after preparation.

Table XII

Product No.	SiO ₂ (%)	Al ₂ O ₃ (%)	Stability (product)	pH (product)
R10-7	10.7	0.4	OK	6.4
R10-12	10.7	0.6	OK	6.1

25 Example 13

In this test series, the polysilicate microgels according to Example 12 were tested for drainage performance as in Example 3 using a similar stock at pH 8.4 and 0.27% consistency, except that no aluminium salt was added separately to the stock. The cationic starch, standard silica sol and order of addition as used in Example 3 were similarly used in this test series.

Table XIII shows the results obtained when adding silica-based materials in varying amounts, in kg/ton, calculated as SiO₂ and based on dry stock system. Without addition of chemicals, the drainage time of the stock was 21.5 sec.

Table XIII

Silica-based		Drainage time (sec) at SiO ₂ dosage of				
	material	0.3 kg/t	0.6 kg/t	1.0 kg/t	1.5 kg/t	2.0 kg/t
	Sol 1	17.0	12.8	9.5	8.5	7.8
5	R10-7	16.5	12.0	9.0	8.0	7.5
	R10-12	16.0	12.2	9.0	7.5	7.5

Example 14

- Polysilicate microgel according to Example 12 was tested for retention performance by measuring the turbidity of the white water obtained by draining stocks according to Example 13. Retention was evaluated according to the procedure of Example 4. Without addition of chemicals, the stock showed a retention value of 97 NTU.

Table XIV shows the results.

Table XIV

Silica-based		Turbidity [NTU] at SiO ₂ dosage of				
	material	0.3 kg/t	0.6 kg/t	1.0 kg/t	1.5 kg/t	2.0 kg/t
	Sol 1	78	60	55	51	46
	R10-7	81	63	56	47	-
	R10-12	72	-	54	49	44

Claims

1. A process for preparing an aqueous polysilicate microgel, characterised in that it comprises mixing an aqueous solution of alkali metal silicate with an aqueous phase of silica-based material having a pH of 11 or less.
- 5 2. A process for preparing high-concentration aqueous polysilicate microgel, characterised in that it comprises mixing an alkali metal silicate solution with an aqueous silica-based material having a pH of 11 or less to prepare an aqueous polysilicate microgel having a SiO_2 content of at least 15%.
- 10 3. A process according to claim 1 or 2, characterised in that the aqueous silica-based material has a pH within the range of from 4 to 11.
4. A process according to claim 1, 2 or 3, characterised in that the aqueous silica-based material has a pH within the range of from 7 to 11.
5. A process according to claim 1, 2 or 3, characterised in that the silica-based material that is mixed with the alkali metal silicate solution is a silica-based sol.
- 15 6. A process according to claim 1, 2 or 3, characterised in that the silica-based material contains aluminium.
7. A process according to any of the preceding claims, characterised in that the alkali metal silicate solution has a SiO_2 content of at least 15% by weight.
8. A process according to any of the preceding claims, characterised in that it further comprises admixing an aluminium salt.
- 20 9. A process according to claim 8, characterised in that the aluminium salt is sodium aluminate.
10. A process according to any of the preceding claims, characterised in that the polysilicate microgel obtained has a molar ratio $\text{SiO}_2:\text{M}_2\text{O}$, where M is alkali metal, between 3:1 and 20:1.
- 25 11. Polysilicate microgel obtainable by a method according to any one of claims 1 to 10.
12. High-concentration polysilicate microgel having a SiO_2 content of at least 17.5% by weight.
- 30 13. Polysilicate microgel according to claim 11 or 12, characterised in that it is aluminated.
14. Polysilicate microgel according to claim 11, 12 or 13, characterised in that it has a specific surface area of at least $1000 \text{ m}^2/\text{g}$.
15. Use of a polysilicate microgel according to any of claims 11 to 14 or prepared by a process according to any of claims 1 to 10 as a flocculating agent in
- 35

combination with at least one cationic or amphoteric polymer in the production of pulp and paper and for water purification.

16. Use according to claim 15, wherein the polysilicate microgel is used as flocculating agent for improving drainage and/or retention in paper making.

5 17. Use according to claim 14 or 15, wherein the polysilicate microgel is used in combination with cationic starch and/or cationic acrylamide-based polymer.

10 18. A process for the production of paper from a suspension of cellulosic fibres, and optional filler, c h a r a c t e r i s e d in that comprises adding to the suspension at least one cationic or amphoteric organic polymer and a silica-based microparticulate material, forming and draining the suspension on a wire, c h a r a c t e r i s e d in that the silica-based material is a polysilicate microgel according to any of claims 11 to 14 or prepared by a process according to any of claims 1 to 10.

15 19. A process according to claim 18, c h a r a c t e r i s e d in that it further comprises adding an aluminium salt to the suspension.

Abstract

The present invention generally relates to polysilicate microgels. More specifically, the invention relates to a process for preparing aqueous polysilicate microgels which comprises mixing an aqueous solution of alkali metal silicate with an aqueous phase of silica-based material having a pH of 11 or less, to polysilicate microgels per se and to the use thereof as flocculating agents in paper making and water purification. The invention further relates to a process for the production of paper from a suspension of cellulosic fibres, and optional filler, which comprises adding to the suspension at least one cationic or amphoteric organic polymer and a polysilicate microgel, forming and draining the suspension on a wire.